PERFORMANCE OF BIMETALLIC SULFIDES WRAPPED WITH GRAPHENE OXIDE FOR ENERGY STORAGE APPLICATIONS

A SYNOPSIS

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1. INTRODUCTION

The rapidly changing lifestyle, escalating fuel scarcity and rising environmental concern have made sustainable, reliable and clean energy source as the greatest quest of the century. Rising demand for portable consumer electronics, quickly growing digital communication media and the need for storing the produced renewable energy insist the need to pinpoint an appropriate energy storage solution. Future's energy sources must be cleaner and much more efficient, flexible and reliable to meet the ever growing worldwide demand for energy. At present, aggravating energy and environmental issues are ringing alarm bells to the human society. Thus, there is an urgent need for enhanced energy security along with reducing greenhouse gas emissions. Global research has focused on the development of sustainable energy storage materials and prototype devices for conversion and storage. The tailor-made engineering solutions in nanomaterial technology play a vital role in energy conversion and storage, because the characteristics of the devices closely depend on the properties of the materials used. Energy storage devices with add-on functionalities have received great interest in many emerging modern electronics such as electronic papers, collapsible displays, and other personal multimedia devices. It requires highly efficient active materials with good electrochemical properties, high mechanical integrity upon bending or folding and lightweight property. This aims to develop advanced electrochemical energy storage devices (EESs) to meet the ever-increasing energy demands. To address the worldwide energy demand and to compete with alternate technologies the high specific power and longer lifetime of supercapacitors serve as an attractive alternate for portable electronics and automotive application. Supercapacitors have gained considerable attention owing to their superior power capability, good safety record, better reversibility and longer cycle life. Their ability to provide larger energy densities than conventional capacitors, higher power densities and longer cycle life than batteries make supercapacitors widely used in fast growing portable electronic devices and in hybrid electric vehicles (HEVs), the need of the hour.

2. LITERATURE SURVEY

Peng et al. [1] grew $NiCo_2S_4$ nanosheets with an average size of about 3.5 nm on the RGO sheets, they showed $NiCo_2S_4$–RGO hybrid electrode presents an extremely high specific capacitance of 1161 Fg^{-1} at 5 Ag^{-1} with uniform distribution and excellent electrical coupling to the underlying graphene sheets and it is maintained at a high value of 1108 Fg^{-1}.

Hou et al. [2] highlighted solvothermal strategy to fabricate monodisperse hollow NiCoSe2 (H-$NiCoSe_2$) sub-microspheres. Pseudocapacitance of ~750 Fg^{-1} at a rate of 3 $Ag^{-1}$with a high loading of 7 $mgcm^{-2}$ after ~100 cyclic voltammetry (CV) cycles. They

analyzed systematic physicochemical/electrochemical and revealed that the electro-oxidation generated bi-active CoOOH/NiOOH phases in aqueous KOH over CV scanning, rather than the H-$NiCoSe_2$itself by the intrinsic energy storage mechanism of the H-$NiCoSe_2$, account for the remarkable pseudocapacitance observed after cycling. They delivered an energy density of ~25.5 $Whkg^{-1}$with a power rate of ~3.75 kW kg^{-1}, and long-span cycle life using an assembled H-$NiCoSe_2$-based asymmetric device.

Hou et al. [3] fabricated high-quality uniform hollow hetero Nio2S4/Co9S8 (NCCS) using hydrothermal. They observed promising electrodes when evaluated for supercapacitors, the resultant hollow mesoporous hetero-NCCS electrode with a mass loading of 5 mg cm^{-2} delivers a fascinating pseudo-capacitance of ~749 Fg^{-1} at a current rate of 4 Ag^{-1}, and it holds approximately 620 Fg^{-1} at 15 Ag^{-1} in virtue of intrinsic synergetic contributions from structural/ compositional/ component merits. Furthermore, achieves an encouraging energy density of around 33.5 Wh kg^{-1} at a power density of 150 W kg^{-1}, and exceptional cycling behaviors with capacitance degradation of ~0.007% per cycle over consecutive 5000 cycles at 5 A g^{-1} an asymmetric device based on hollow mesoporous hetero-NCCS.

Yu et al. [4] demonstrated a facial method for the synthesis of $NiCo_2S_4$/graphene composite where $NiCo_2S_4$is encapsulated with an ultrathin graphene layer to form a core/shell structure ($NiCo_2S_4$@G). They obtained that the $NiCo_2S_4$@G composite has excellent electrochemical performance with a specific capacitance of 1432 Fg^{-1} at a current density of 1 Ag^{-1}. They synthesized a hybrid supercapacitor assembled using the $NiCo_2S_4$@G as a positive electrode and porous carbon as a negative electrode that demonstrates a high energy density of 43.4 Wh kg^{-1} at a power density of 254.3 W kg^{-1} in the voltage range 0-1.35 V. They reported that after 5000 charge/discharge cycles, the device still retains 83.4% of its initialcapacitance.

Pramanik et al. [5]reported growth of carbon-doped ZnCo2S4 directly on Ni foam by solvothermal. They tested faradaic electrode vs Pt in 3.0 M aqueous KOH electrolyte, remarkably high specific capacity of 1282.5 Cg^{-1} (356.2 $mAhg^{-1}$) could be realized at a current density of 1.0 Ag^{-1}. They developed hybrid ZnCo2S4//KOH//AC cells which exhibit a commendable performance with an energy density of 101.4 W h kg^{-1} at a power density of 1.3 kW kg^{-1}. They reported that even after a 50-times increase in the current density (power density 57.5 kW kg^{-1}), the hybrid cell could still retain an energy density of 40.4 Wh kg^{-1} outperforming other metal oxides/sulfide//AC-based hybrid supercapacitors.

Xu et al. [6] prepared the amorphous $CoMoS_4$ using a simple precipitation method.

They obtained that in a three-electrode system, the ratio capacitance of a $CoMoS_4$ sample can gain 661 F g^{-1} at a current density of 1 Ag^{-1}. They highlighted the application of $CoMoS_4$, the $CoMoS_4$ symmetric device that shows the ratio capacitance of 142 Fg^{-1} at 2 Ag^{-1}; the assembled $CoMoS_4$//rGO hybrid supercapacitor also owns a high ratio capacitance of 68 F g^{-1} at 1 Ag^{-1} with energy and power densities of 27.2 Wh kg^{-1} at 400 W kg^{-1} and 17 Wh kg^{-1} at 2400 W kg^{-1}. Further, the hybrid supercapacitor has good capacitance retention (86% after 10000 cycles), and low internal and Warburg resistances.

Panet et al. [7] synthesized novel rGO@$CuCo_2S_4$@CoS_2/NF composite material with core-shell structure by ZIF-67 derivatives and the solvothermal method. Then they reported that the rGO@$CuCo_2S_4$@CoS_2/NF electrode that exhibits an excellent specific capacity is 2447.1 Fg^{-1} (1101.2 Cg^{-1}) at a current density of 1 Ag^{-1} and with 79.2% of the initial value they got outstanding cycling performance after 10,000 cycles. they designed a typical asymmetric supercapacitor (ASC) device based on rGO@$CuCo_2S_4$@CoS_2/NF as the cathode and AC as the anode (rGO@$CuCo_2S_4$@CoS_2/NF) that achieves a maximum energy density of 52.46 $Whkg^{-1}$with the power density of 750.02 W kg^{-1}. Moreover, they reported that the device maintains a cycle stability of 88.2% after 10,000 cycles, and demonstrated that the rGO@$CuCo_2S_4$@CoS_2/NF could be a potential electroactive material in advanced energy storage systems.

Pan et al. [8] prepared NiCo2S4@NiV-LDH/NF composite material with a core-shell nanostructure through a simple hydrothermal method. Alongwith, they synthesized NiCo2S4@NiV-LDH with varying NF by adjusting the sulfur concentration. They reported a specific capacity of 1778.8 C g^{-1} (3557.6 F g^{-1}) at 1 A g^{-1}. They noted that, under the condition of a power density of 749.98 W kg^{-1}, the energy density of the $NiCo_2S_4$@NiVLDH/NF-2//BC device was 120.81 Wh kg^{-1}. They reported that the low detection limit of $NiCo_2S_4$@NiV-LDH/GCE sensor was 0.46 μM, the wide linear range was 0.5–153 μM, and the highest sensitivity.

Guan et al. [9] synthesized the hierarchical NiS micro flowers using Ni(OH)2 as precursors through the sulfuration process. They revealed that from electrochemical characterization the NiS presented high specific capacitance in 3 M KOH electrolyte (1122.7 Fg^{-1} at the current density of 1 Ag^{-1}) and good electrochemical cycling stability (97.8% of the specific capacitance is retained after 1000 charge-discharge cycles at the current density of 10 Ag^{-1}). They observed that an asymmetric supercapacitor with NiSas the positive electrode and activated carbon as the negative electrode delivered a high energy density of 31 Wh kg^{-1} at a power density of 0.9 kW kg^{-1} under an operating voltage window of 1.8 V.

Pan et al. [10] highlighted that the Metal-organic frameworks (MOFs)-based derivatives provide a flexible platform for constructing high-performance supercapacitors as electrode materials. They successfully prepared a novel $NiFe_2O_4/NiCo_2O_4$/GO composite using dual-MOF as the precursor. They found that the $NiFe_2O_4/NiCo_2O_4$/GO composite formed a special structural morphology and also provided a large surface area. They reported that the composite electrode material exhibited an excellent specific capacity of 661.6 C/g (1470 Fg^{-1}) at 1 Ag^{-1}, excellent rate capability (from 1 to 20 Ag^{-1} the specific capacity decreases about38%), and outstanding long cyclic life (89.9% capacity retention after 3000 cycles). Moreover, an asymmetric supercapacitor was composed of $NiFe_2O_4/NiCo_2O_4$/GO and activated carbon as positive electrodes and negative electrodes, respectively. Meanwhile, ASC exhibited a specific capacity of 373.3 Cg^{-1} at 1 Ag^{-1} in a potential range from 0 to 1.45 V, it showed Journal Pre-proof the maximum energy density of ASC equal to 109 Wh kg^{-1} at a power density of 1051.17 W kg^{-1}. In addition, the $NiFe_2O_4/NiCo_2O_4$/GO//AC has outstanding cycling stability (90.7% capacitance retention after 1000 cycles), which makes it a potential application in the field of energy storage-conversionapplication.

Wu et al. [11] fabricated flexible yolk-shelled $NiCo_2S_4$ hollow spheres/reduced graphene oxide (RGO) hybrid lamellar films by developing a facile strategy of vacuum filtration. They monitored that the as-prepared $NiCo_2S_4$/2RGO hybrid lamellar films with excellent conductivity delivered appreciable capacitance of 1000.5 F g^{-1} at 1 A g^{-1}. Moreover, They synthesized the asymmetric supercapacitor (ASC) successfully by utilizing the activated carbon (AC) and $NiCo_2S_4$/2RGO hybrid lamellar films as the negative electrode and positive electrode, which manifested a high energy density of(15.4 Wh kg^{-1} at a power density of 2227.3 W kg^{-1}coupled with remarkable cycling stability which has retention of 80.5% over 5000 cycles.

Guan et al. [12] developed a sequential ion-exchange approach for preparing complex onion-like $NiCo_2S_4$ particles with hollow structured shells. After the sequential ion-exchange reactions with S_{2-} and Ni_{2+} ions, they obtained onion-like Co_3O_4 particles with solid shells, and complex onion-like Co_3O_4 and $NiCo_2S_4$ particles with unique hollow structured shells respectively. They benefited from the unique shell architecture and robust matrix, the as-prepared onion-like $NiCo_2S_4$ particles exhibit superior electrochemical performance for hybrid supercapacitors with outstanding cycle life and enhanced energy and power densities.

Hoa et al. [13] fabricated a three-dimensional reduced graphene oxide / nickel-cobalt sulfide (RGO/$NiCo_2S_4$) aerogel by an efficient and facile one-step hydrothermal approach. They designed exaAs an active electrode material for supercapacitors, the RGO/$NiCo_2S_4$

aerogel exhibited a large capacitance of 813 F g^{-1} at 1.5 A g^{-1}. They examined that the asymmetric supercapacitor (RGO/ $NiCo_2S_4$ aerogel // RGO) showed a Cs of 45.3Fg^{-1} at 1.0 A g^{-1} and a suitable remaining capacitance of over 84.3% after 2000 cycles which had a highenergydensityof40.3Whkg^{-1}at375.0Wkg^{-1}andapowerdensityof26.2kWkg^{-1}at3.7 kWh kg^{-1}. They suggested this device has great potential applications in energy storage.

Ma et al. [14] fabricated three-dimensional sulfur-doped graphene supported by nickel-iron bimetallic sulfides ($NiFeS_2$/3DSG) as high-performance supercapacitors electrode by one-step microwave alcohothermal method. $NiFeS_2$/3DSG electrode has reflected in the specific capacitance of 643.9 C g^{-1} (1073.2 F g^{-1})at the current density of 1Ag^{-1} in 6.0 M KOH electrolyte. Furthermore, they constructed the asymmetric supercapacitor device of $NiFeS_2$/3DSG electrode as the positive electrode and 3DSG as the negative electrode ($NiFeS_2$/3DSG//3DSG), which delivers a superior energy density of 45.7 Wh kg^{-1} at a power density of 222 W kg^{-1} under a wide potential range of 1.6 V. They monitored CV and GCD, After 5000 cycles of charge and discharge, the specific capacitance of this device holds the retention rate of 82%.

Mohamed et al. [15] fabricated Carbon-containing $NiCo_2S_4$ hollow-nanoflake structures by a one-step solvothermal method using CS_2 They reported that the $NiCo_2S_4$nanoflake electrode exhibited a high specific capacitance of 1,722 F g^{-1} with a specific capacity of 688.8 C g^{-1} at a current density of 1 A g^{-1} and an excellent cycling stability with capacity retention of 98.8% after 10,000 cycles. They fabricated an asymmetric supercapacitor based on $NiCo_2S_4$ nanoflakes and activated carbon electrodes revealed a high energy density of 38.3 Wh kg^{-1} and a high power density of 8.0 kW kg^{-1} with capacitance retention of 91.5% and coulombic efficiency of 95.6% after 5,000 cycles.

Chen et al. [16] synthesized self-standing $NiCo_2S_4$ nanotube arrays which have been in situ grown on Ni foam by the anion-exchange. They observed that the $NiCo_2S_4$ nanotube arrays hybrid electrode exhibits an ultrahigh specific capacitance of 14.39 F cm^{-2} at 5 mA cm^{-2} with excellent rate performance with the 67.7% retention for current increases 30 times and cycling stability with 92% retention after 5000 cycles at a high mass loading of 6 mg cm^{-2}. They can achieved high areal capacitance of 4.68 F cm^{-2} at 10 mA cm^{-2}, high energy density of 31.5 Wh kg^{-1} at 156.6 W $kg^{-1}$and high power density of 2348.5 W kg^{-1} at 16.6 Wh kg^{-1} by assembling asymmetric supercapacitor with reduced grapheme oxide at a total active material mass loading as high as 49.5 mg^{-1}.

Wanget al. [17] synthesized unique amorphous bimetallic sulfides of $CoNi_2S_4$with nanocage structure. First, they synthesized ZIF-67 with typical rhombic dodecahedron

structure. Their results revealed that the synthesized $CoNi_2S_4$ nanocages have low charge transfer resistance, and high specific capacitance of 1890 F g^{-1} at a current density of 4 A g^{-1}. They observed that the specific capacitance remains 89.9% and 71.6%, respectively after 1000 and 5000 cycling charge-discharge measurements. Furthermore, they fabricated an asymmetric supercapacitor which assembled using $CoNi_2S_4$ nanocages as positive electrode materials and Yolk-Shell carbon spheres (YS-CS) as negative electrode materials, and they observed that the resulting $CoNi_2S_4$//YS-CS device exhibits a high energy density of 35 Wh kg^{-1} at a power density of 640 Wkg^{-1}.

Chang et al. [18] fabricated the novel material, $ZnCo_2O_4$/C microspheres in a yolk-shell structure by a facile refluxing process in combination with a calcination treatment. They observed this material exhibits remarkable electrochemical properties such as high specific capacitance of 1821 F g^{-1} at 5 A g^{-1}), excellent rate performance, superior cycling stability with no capacitance loss over 9000 cycles. They assembled an asymmetric supercapacitor coupled with an active carbon anode that can deliver a high energy density of 45.9 Wh kg^{-1} at a power density of 700 W kg^{-1} with an excellent cycling stability with a capacitance retention rate of over 95% after 9000 cycles

Xu et al. [19] fabricated the asymmetric supercapacitor with a hollow $NiCo_2O_4$ nanospheres electrode and activated carbon electrode as the positive and negative, respectively. They reported that the device has maximum energy density of 21.5 Wh/kg, excellent cycling performance and coulombic efficiency. Their results showed that the hollow $NiCo_2O_4$ nanosphere electrode is a promising electrode material for future application in high-performance supercapacitors.

Zeng et al. [20]fabricated three-dimensional (3D) hollow CoS_2nanoframes (HCSN) by partial anion replacement of Co-based Prussian blue (PB) nanocubes. They observed that the as-synthesized 3D HCSN exhibit l good electrochemical performances including a high specific capacitance of 568 F g^{-1} at 0.5 A g^{-1} and good cycling stability with 88.3% specific capacitance retention after 5000 cycles. They fabricated the asymmetric supercapacitor from the 3D HCSN that can present a high energy density of 32.3Wh kg^{-1} at a power density of 4 $kWkg^{-1}$. They promoted 3D HCSN for good structural stability and low density, further promoting their potential application in high-performance supercapacitors.

3. OBJECTIVE

The following are the main objectives framed for the research

- To prepare pure nanocomposites, bimetallic sulfides, and Graphene oxide using the hydrothermal method.

- To characterize the prepared nanocomposites using XRD, FESEM, HRTEM, XPS, CV, and GVD.
- To analyze the materials and methods for enhancing the performance of energy storage devices
- To enhance the performance of energy storage devices by improving the specific capacitance, power density, and Energy density due to the addition of different ratios of GO on Bimetallic Sulfides.

4. RESEARCH PROBLEM

The properties of nanocomposite electrodes depend not only upon the individual components used but also on the morphology and the interfacial characteristics. Recently, considerable efforts have been placed to develop all kinds of nanocomposite capacitive materials, such as mixed metal oxides, conducting polymers mixed with metal oxides, carbon nanotubes mixed with conducting polymers, or metal oxides, and graphene mixed with metal oxides or conducting polymers. Design and fabrication of nanocomposite electroactive materials for supercapacitors applications needs the consideration of many factors, such as (i) material selection, (ii) synthesis methods, (iii) fabrication process parameters, (iv) interfacial characteristics, (v) electrical conductivity, (vi) nanocrystallite size, and (vii) surface area, etc. Although significant progress has been made to develop nanocomposite electroactive materials for supercapacitor applications, there are still a lot of challenges to be overcome.

In comparison to other carbonaceous materials, graphene oxide (GO) is hence a material that is widely used for charge storage applications in supercapacitors. It is due to their excellent properties like (i) high electrical, (ii) mechanical, (iii) thermal conductivity, (iv) chemical stability and (v) vast surface area.

Owing to the aforementioned advantages of nanocomposites and graphene oxides, In this thesis, we try to put practical solutions of the global energy crisis with minimizing the environmental impacts from a materials researcher's perspective. We tried Major thrusts are given to make the synthesis of materials of interest simpler and the fabrication methods economic and industrially applicable. The prepared electrode materials have been subjected to various structural, compositional, morphological and textural properties. All the fabricated bimetallic sulfides electrodes have been tested systematically for their electrochemical performance like cyclic voltammetry (CV), galvanostatic charge discharge (GCD) and electrochemical impedance spectroscopy (EIS) in a three-electrode system. Various electrode geometries are also experimented, and a 3-dimensional (3D) geometry is identified as an ideal one for making high power density and energy density storage devices. The overall

performance of the synthesized electrode materials is assessed in comparison with those reported in the literature.

5. ORGANIZATION OFTHESIS

This thesis work preferentially motivates us to investigate intriguing electrochemical energy storage performance of some innovative Metal (M)-Transition metal(TM) bimetallic sulfides wrapped on GO nanocomposite which have been rarely studied so far. The enhanced properties of the as-synthesized M-TM-GO nanocomposites have been explained in terms of synthesis techniques, hierarchical surface morphology, electrode and electrolytic properties, and process control. The aforementioned work has been described systematically in seven chapters as follows:

Chapter 1 accentuates the introduction of energy storage devices and their application. It includes the classification of energy storage devices. Types of supercapacitors are reported. The role of sulfides in supercapacitors is reported. It introduces the role of different sulfides and the synthesis of their nanostructure. Applications of energy storage devices using sulfides are also reported. It highlights the elaborate description and working principle of supercapacitors.

Chapter 2 reports the literature survey of various sulfides and oxides in the field of energy storage devices. It also includes the present work relevant to the scope of the research thesis. Metal Oxides are widely used materials for supercapacitors. The survey reports that sulfides are treated equally in the field of supercapacitors and it has higher power density and energy density same as metal oxides. In the survey specific capacitance, retention with cycles, power density, energy density, and its applications is discussed.

Chapter 3 brings up the characterization techniques and synthesis of nanocomposites. It describes various synthesis procedures for preparing sulfide nanocomposites such as coppercobalt sulfide, Nickel cobalt sulfide, and Zinc Cobalt Sulfide. It also provides the various methodologies used to fabricate the electrode and prepare the electrolyte. Along with this, characterization equipment for analysis of the structural, morphological, and electrochemical performance of sulfide nanocomposites is also discussed.

Chapter4 describes sunflower petal-shaped $CuCo_2S_4$@GO was prepared by a simple hydrothermal method and serves as an active electrode to analyze for supercapacitor applications. FESEM images show that the wrapping of GO on the surface of Cu Co_2S_4shows petal shaped needle-like structure with minute pores in it. It is noted that GO-wrapped $CuCo_2S_4$ delivers excellent electrochemical performance with a specific capacitance of about 900 Fg^{-1} with a capacity retention of about 80% after 5000 cycles. And also

asymmetric capacitor was fabricated by using $CuCo_2S_4$@GO(3%) and AC as the positive and negative electrodes and delivers the higher energy and power density (47.2 $Wh \cdot kg^{-1}$, 0.896 $kW \cdot kg^{-1}$) and long cycling stability after 10,000 cycles. The electrochemical performance shows that$CuCo_2S_4$@GOwillbeagreatelectrodeforenergystorageapplications.

Chapter 5 describes the growing demand for an energy storage device with higher performance electrochemical supercapacitors that attracts huge attention to their performance. High capacity and high energy density are the primary goals of supercapacitor devices. Recently extensive research is carried out on $NiCo_2S_4$ which acts as a promising material for supercapacitor applications. In the present work, 3D hierarchical $NiCo_2S_4$ will be prepared through the hydrothermal method. To enhance the electrochemical performance of $NiCo_2S_4$, $NiCo_2S_4$ will be anchored on GO at the surface level which delivers high-capacity retention during long-term cycling. For the preparation of pure $NiCo_2S_4$, Nickel nitrate and cobalt nitrate will be used as fundamental precursors. Thiourea will be used as a sulfur source. After the preparation of pure material, GO will be coated on pure material using the solid-state method. After the preparation XRD, FESEM, and HRTEM analysis was taken for the confirmation of the phase and morphological status of the sample. A detailed CV and GCD analysis was performed for understanding the electrochemical performance of the electrodematerial.

Chapter 6 highlights the great energy density that supercapacitors provide is in critical demand right now. In this work, flower-like nano-flakes are shaped $ZnCo_2S_4$@GO by hydrothermal method. $ZnCo_2S_4$@GO is used because of its large electroactive surface area, flower-like morphology, and quick channels for ion diffusion and electron transport in the as-prepared hierarchical arrays. The GO-coated $ZnCo_2S_4$ delivers a capacity of about 1095 Fg^{-1} at 1 Ag^{-1}. An asymmetric supercapacitor is fabricated with the assembly of $ZnCo_2S_4$@GO(3%) as the positive electrode and CNT as a negative electrode, which delivers a capacity of about 164 Fg^{-1}. The ASC delivers a high energy density of about 138Wh kg^{-1} with a power density of 2810 W Kg^{-1} with a capacity retention of 95% after 10,000 cycles. The better electrochemical results show that $ZnCo_2S_4$@GO will be suitable for energy storageapplications.

Chapter 7 describes the summary of the research carried out in this thesis to highlight the better-performing bi-metallic sulfide nanocomposites from the investigated research. From this work, anyone is able to understand the usefulness of the electrode materials and analyze the observed enhancements.

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LIST OF PUBLICATIONS

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